Conference Paper

# Investigation of Viscose Rayon Manufacturing Sludges, Considered as a Raw Material for Zinc Production

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## Abstract

At treatment of wastewater of viscose rayon's spinning produces the sediment – zinc-bearing sludge, a humidity content of 66 to 95 %. To date, it is deposited up to 2.5 million cubic meters of zinc-bearing sludge in the ponds of plants in Russia. In the paper chemical composition and particle size distribution of sludge of viscose rayon manufacturing (OJSC "Balakovskoye khimvolokno", OJSC "Ryazanskoye khimvolokno", OJSC "Sibvolokno") are presented. The percentage of zinc in sludge is of 6 to 23 %. Investigations by methods of X-ray diffraction (XRD) and scanning electron microscopy (SEM) are shown, that zinc is present in form of hydroxides, carbonates and silicates. Thermodynamic analysis of zinc dissolution of compounds, found in product of sludge roasting at a temperature of 850°C, was conducted.

**Keywords:** Zinc-bearing sludges, viscose, rayon manufacturing wastes, structure, zinc leaching

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## 1. Introduction

At rayon plants the concentrated solution of zinc sulphate for viscose rayon spinning is using. Every year up to 20 000 tons of zinc as sulphate are spent for this purpose. Wherever the solution becomes polluted it is neutralized and being dumped to the pond. Zinc almost totally precipitates out, becoming a component of sludge [1].

Wastewaters neutralization is made by natural limestone or by lime milk. For decades, a lot of zinc was deposited in lime-gypsum sludges. For example, ponds of "Balakovskoye khimvolokno" is containing 2700 thousand tons of sludges, "Ryazanskoye khimvolokno" has 160 thousand tons, "Sibvolokno" has 80 thousand tons of sludges. Percentage of zinc in sludges (by dry weight) is of 6 to 23%. Sludges humidity, depending on the depth reaches 70-80%. The most of zinc (53% of total) is concentrated in ponds of Balakovo's production association "Khimvolokno". For the construction of new ponds, it is necessary to have a lot of area that is not available for rayon plants.

| Particle size, mm | Containing, % |
|---|---|
| +2.5 | 3.1 |
| +1.0 | 7.7 |
| +0.2 | 20.3 |
| +0.05 | 10.7 |
| -0.05 | 58.2 |

Table 1: Particle size distribution of sludge.

| Zn | Ca | Fe | Cu | Al | S. | $SiO_2$ | C |
|---|---|---|---|---|---|---|---|
| 6.3–23.5 | 6.5–10.6 | 0.9–1.7 | 0.03 | 0.6–1.6 | 5.7–6.4 | 5.1–21.8 | 10.5–10.6 |

Table 2: Chemical composition of sludges of viscose rayon manufacturing plants ("Balakovskoye khimvolokno", "Ryazanskoye khimvolokno", "Sibvolokno"), to dry weight, %.

## 2. Results and Discussion

It is known some methods of treatment of the sludges, that have pros and cons [2–4]. Treatment of the sludges of viscose rayon manufacturing wastes could be applied as a raw material for UMMC's zinc plants, particularly, OJSC "Electrozink" and "Chelyabinsk Zinc Plant". Wet sludge has grey color, humidity of 66 to 95%, volumetric mass of 0.68 to 1.35 g/dm$^3$. In air-dried product the solid particles inspired and bound by thin and weak cellulosic fibres. Losses in roasting (at 750°C) represents 25%. Volumetric mass of the sludge, being dried at 105°C, is 0.49 g/dm$^3$, density – 2.36 g/dm$^3$, average specific surface area of particles – 2226 cm$^2$/g. The results of wet screening of sludge is presented in the Table 1.

Chemical composition of sludges presents as an averages of enterprise laboratories' reports of different plants (Table 2). X-ray crystallography of sample of sludge from "Balakovskoye khimvolokno" was conducted by "DRON-3" diffractometer in the range of angle 15-95° with copper anode, X-ray powder diffractogram is presented on Figure 1. The most significant peaks on the diffractogram belong to the following species: $SiO_2 \cdot 0{,}14H_2O$, $SiO_2$, $Zn_5(OH)_6[CO_3]$, $CaCO_3 \cdot 2H_2O$, $[ZnOH]_2SO_4$ and $FeO(OH) \cdot 4H_2O$. High intensity of peaks, marked 3 and 4 (hemimorphite and gypsum) suggest that there is high content of the compounds. Method of neutralization of wastewaters by natural lime is explaining the presence of zinc hydrocarbonate. Lepidocrocite (FeOOH) additive incomes, probably, within the lime.

Investigation of structure of zinc-bearing sludge samples was conducted using transmission electron microscope (JEM 2100) with additional analytical equipment Oxford Inca. Feature of the tool is option of combination of visual spectrum of particles and its chemical composition in the outcome. Multiphase structure of the sludges of viscose rayon manufacturing is confirmed. Results are presented on Figure 2. According

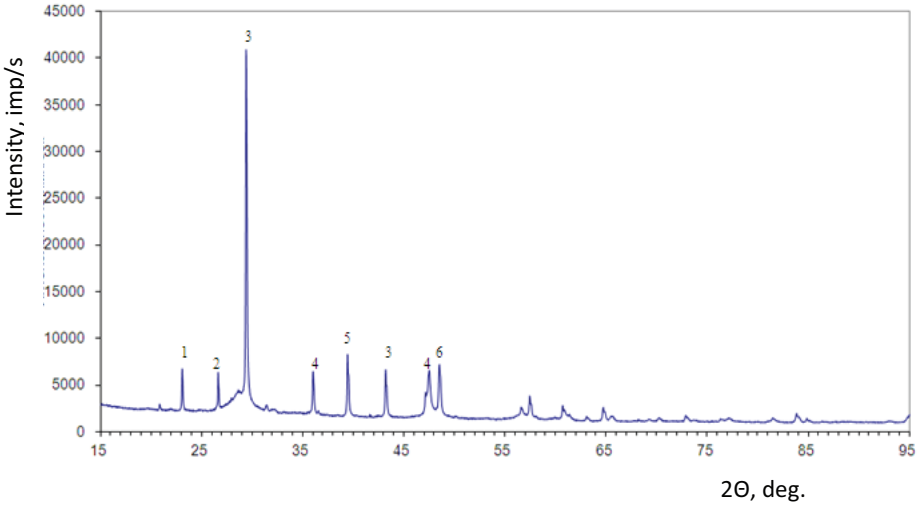


**Figure** 1: Diffractogram of the original sample of sludge: 1 – $SiO_2 \cdot 0{,}14H_2O$; 2 – $SiO_2$; 3 – $Zn_4Si_2O_7(OH)_2 \cdot H_2O$; 4 – $CaCO_3 \cdot 2H_2O$; 5 – $[ZnOH]_2SO_4$; 6 – $Zn_5(OH)_6[CO_3]$; 7 – $FeO(OH) \cdot 4H_2O$.

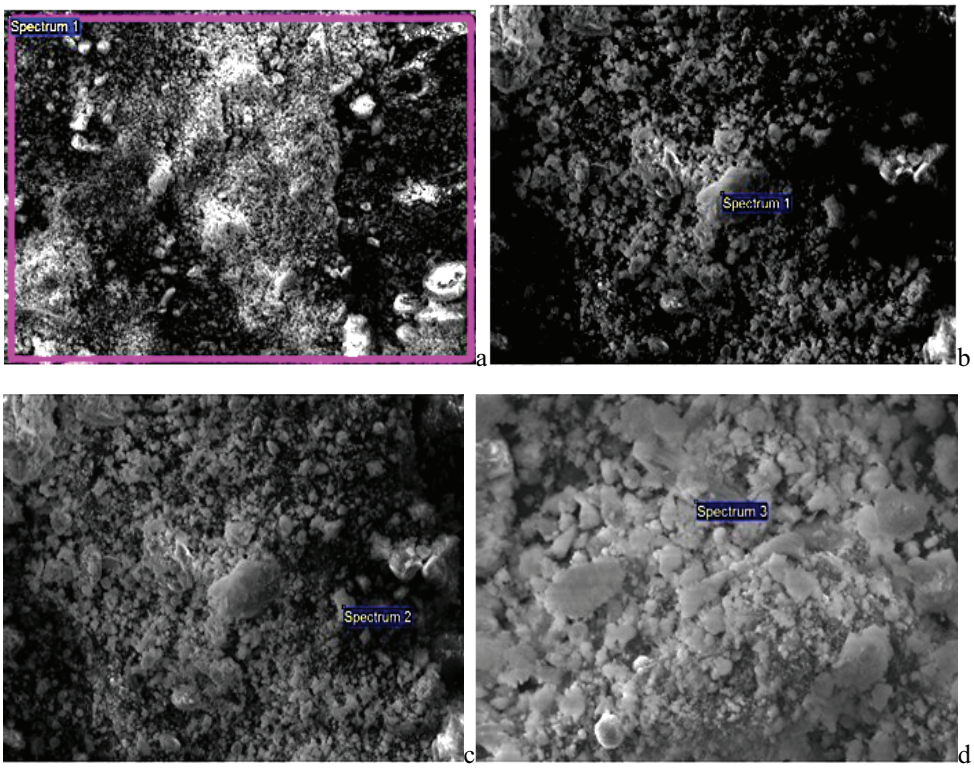


**Figure** 2: Sludge's particles structure: a – common spectrum; b, c and d – individual particles spectrum.

to results of chemical analysis the main elements of the sample (original sludge) is, %: 17.44 Ca, 14.5 Zn in combination with silica (5.17 %) and oxygen (45.33 %). Comparing with XRD analysis it may be assumed that $SiO_2$, $SiO_2 \cdot nH_2O$, $CaCO_3 \cdot 2H_2O$

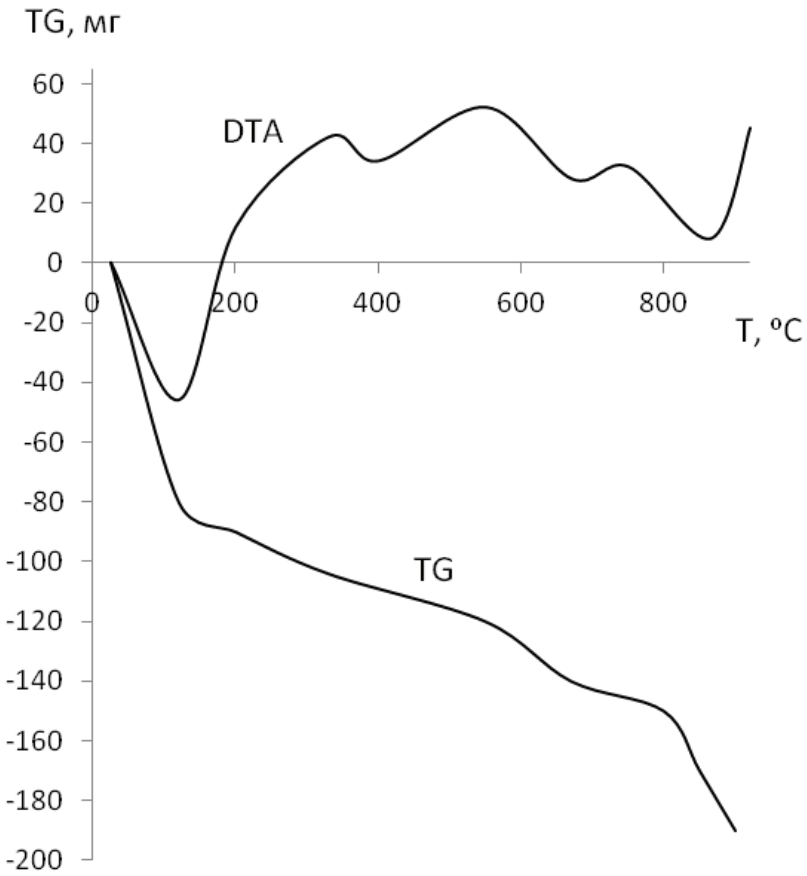


**Figure** 3: Heat pattern of sludge roasting.

In spectrum of area "1" (Figure 2, b) lines of silica (11.42 %) and iron (14.56 %) in combination with oxygen (40.68 %) and calcium (4.23 %) and zinc (8.86 %), that is corresponds to presence of $SiO_2 \cdot 0{,}14H_2O$, $SiO_2$, FeOOH, CaO, $[ZnOH]_2SO_4$. In area "2" (Figure 2, c) sulfur (6.43 %), zinc (22.4 %), silica (13.02 %) in combination with oxygen (39.33 %) and iron (4.29 %). As a trace metals magnesium and aluminum are presence. According to the XRD analysis $Zn_5(OH)_6[CO_3]$, $SiO_2$, FeOOH, MgO, $Al_2O_3$ was defined. In spectrum of area "3" (Figure 2, d) lines of zinc (23.59 %) and sulphur (10.14 %) in combination with oxygen (39.63 %), that is corresponds to presence of $[ZnOH]_2SO_4$. Traces of magnesium and aluminum was identified. Compounds discovered: MgO, FeOOH.

Investigation of thermal decomposition of organics is due to presence of viscose and natural fibers in sludge. A thermogravimetric analysis of sludge shown the mass loss at temperature more than 120°C (Figure 3), that is caused by sample's dehydration. There is an emission of carbon dioxide by the calcium carbonate decomposition and burning of organics in the range of temperature 550-900°C. Total mass loss is made up 57 %.

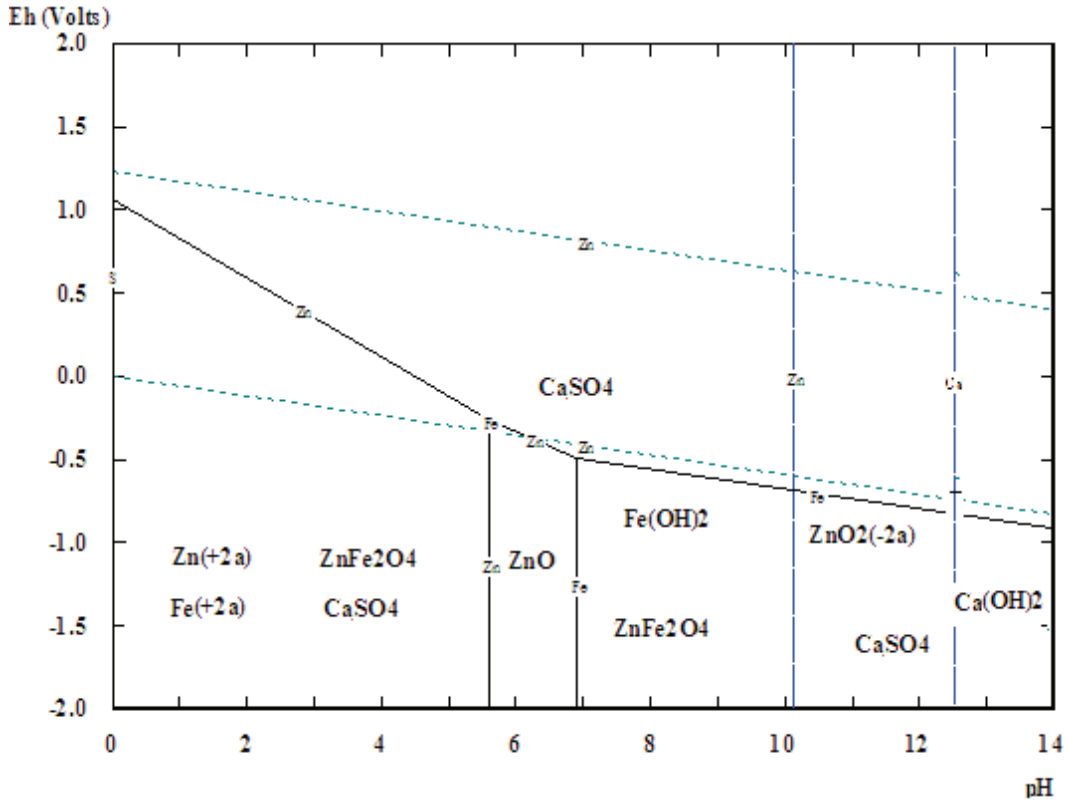


**Figure** 4: Pourbaix diagram of Zn-Fe-Ca-S-$H_2O$ system.

Diagram of differential thermal analysis shows endothermic reactions at 122, 389 and 671°C. This corresponds to crystallization water, $OH^-$ groups and calcium carbonate decomposition. Significant endothermic effect at 865°C and dramatic mass loss is due to the burning of organics. Thus, preliminary roasting of sample should be conducted at temperature 800-900°C to constant weight. In product of roasting, by XRD analysis, following compounds $Ca(OH)_2$, $Zn_2SiO_4$, ZnO, $Fe_2SiO_4$ и CaO.

Composition of roasting product allows to guess following reactions during leaching:

$$Zn_2SiO_4 + 2H_2SO_4 = 2ZnSO_4 + SiO_2\downarrow + 2H_2O \quad (1)$$

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \quad (2)$$

$$Ca(OH)_2 + H_2SO_4 = CaSO_4\downarrow + 2H_2O \quad (3)$$

$$CaO + H_2SO_4 = CaSO_4\downarrow + H_2O \quad (4)$$

$$Fe_2SiO_4 + 2H_2SO_4 = 2FeSO_4 + SiO_2\downarrow + 2H_2O \quad (5)$$

Pourbaix diagram of Zn-Fe-Ca-S-$H_2O$ system shows presence of ions and molecules: in acidic solution it is probably to dissolution of Zn and Fe from zinc oxide and ferrite.

In the range of pH 5.5–7.0 iron and zinc hydroxides are formed (Figure 4). Calcium sulphate crystallization take place in long range of pH. Thus, new solid phase is formed. In diagram, presence of silicates, that forms insoluble compounds in acidic solution is not considered. In this context, after leaching of sludge it expected to form following products:

1. Zinc sulphate solution with impurity of iron sulphate;
2. Calcium sulphate sediment in mixture with insoluble silica $SiO_2$.

## 3. Conclusion

Zinc-bearing sludges of viscose rayon manufacturing is a promising multitonnage anthropogenic raw material for zinc industry.

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